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Effect of sucralose on browning reaction in sucrose/sucralose/lysine model system

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ABSTRACT

Concentrated Chicken Soup (CCS) contains high amount of amino acid and normally sucrose is added to improve flavor. This leads to color change due to Maillard reaction during storage of CCS. This study aimed to study the effect of sucralose on browning reaction in CCS. The CCS system was complex. Therefore, sucrose/lysine was used to investigate the kinetics of browning reaction during heat treatment. Sucralose is sweeter than sucrose 450 times. So, using sucralose could reduce the uses of sucrose in higher amount. In model system, the concentration of lysine was available in excess and sucrose was a limiting substrate. Sucrose content was decreased by 0, 50 and 100% w/w of its original concentration while sucralose was added at an equivalent sweetness. Brown color formation (A_{420}) , pH, color development (L*,a*,b*) and sugar content (sucrose, glucose and fructose) were monitored at time intervals during heat treatment at 70, 80, 90 and 100°C. The result indicated that the increase of temperature, sucrose concentration and heating time resulted in the increasing of A₄₂₀, color development, the accumulation of glucose and fructose content. However, the pH value of the system was constant throughout the studies. Sucralose could be a cause of browning reaction. Zero-order reaction in series kinetics model could be used to describe brown color formation, loss of sucrose, accumulation of glucose and fructose during heat treatment. Temperature dependence of the rate constants of sucrose and fructose reduction and brown color formation could be described by exponential equations. Linear equation was used to describe the temperature dependence of the rate constant of the reduction of glucose.

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INTRODUCTION

Nowadays, urban working life has been changed. People spend more time on transportation and less time on meal preparation. Therefore, pre-cooked or partially prepared food becomes more popular. Concentrated chicken soup (CCS) can be used as a good base for various dishes. It helps shorten cooking time and increases the taste of foods. However, during storage at room temperature, the color of CCS changes from light brown to dark brown which is unaccepTable by consumers.

Browning reaction is the major cause of color change in many food products. The cause of browning reaction in CCS may come from either ingredients or processing condition. CCS is prepared by mixing between concentrated chicken stock and ingredients and pasteurizing. As CCS is heated at high temperature, enzymatic browning reaction is not likely to be a major cause of browning reaction. Various ingredients in CCS such as sugar from seasoning, soy sauce and sugar from chicken stock and lipid from chicken stock could cause browning in CCS. Thus, Maillard reaction is likely to be a main cause of browning in CCS because of its high concentration of sugar and amino acid.

Maillard reaction is a reaction between mono-saccharides and amino acids or proteins. The product of this reaction is the brown pigment called melanoidins (Martin and Van Bockel, 2005a). The rate of Maillard reaction and type of products formed depends on many factors, including temperature, water activity, pH, type and concentration of reactants (Matmaroh *et al.*, 2006).

In CCS, the concentration of amino acid is high amount due to the nature of the product. The water activity, pH and process temperature of CCS cannot be adjusted due to the product and processing specification. Thus, this research focuses on the effect of sugar (sucrose) on Maillard reaction. Decreasing of sucrose concentration could decrease the rate of Maillard reaction because sucrose could break down to glucose and fructose which are a major precursor of melanoidins (Matmaroh *et al.*, 2006). Therefore, this work proposed to replace sucrose with sucralose while maintained the level of sweetness of the product.

Several researchers studied the effect of sucralose on sensory properties and physical properties in fruit juice (Al-Dabbas *et al.*, 2012; Cadena *et al.*, 2013). It was found that sucralose gave a good acceptance level similar to that of the product using sucrose and no effect on health was found. However, there were no studies of the effect of sucralose on browning reaction. Therefore, this work aims to investigate the effect of sucralose on browning reaction (Maillard reaction) in CCS. However, CCS system was rather complex. Therefore, sucrose/sucralose/L-lysine system was used as a model system to study the CCS system performance and the kinetic of sugar and melanoidins changes in the system. L-lysine was used in the system due to the high reaction rate than others amino acid (Rattanapanone 2008).

MATERIALS AND METHODS

Chemicals

D-glucose, D-fructose, D-sucrose and L-lysine were purchased from Sigma-Aldrich (Germany). Milli Q-water (HPLC glade) was purchased

from Lab-scan Ltd. (Thailand). Sucralose was obtained from nutrition Sc. (Thailand).

Preparation of sucrose-sucralose-lysine model system

The model system was prepared by using lysine, sucrose and sucralose. The concentration of lysine, sucrose and sucralose were shown in Table 1. The concentration of lysine was fixed at 0.05 M which is 10 times to sugar concentration. So, the L-lysine in the system was excess which was similar to the real CCS system. The concentration of sucrose was decreased by 50 and 100% by weight and was replaced by sucralose. The amount of sucralose (sucrose substitute) was calculated by using the sweetness value of sucralose which is 450 times sweeter than sucrose. The pH of the model system was adjusted to pH 6 by using 1.0 N of HCl. The samples were filled in the screw capped glass tube and heated at 70, 80, 90 and 100°C in oil bath, respectively. The pH, browning pigment formation (A_{420}), L^{*},a^{*} and b^{*} values and sugar content of the samples were determined at time intervals during 48 hours of heating. Each reaction mixture was prepared, heated and analyzed in duplicate.

 Table 1
 The concentration of L-lysine, sucrose and sucralose in model system.

Samples	L-lysine	Sucrose	Sucralose
	(Molar)	(Molar)	(Milimolar)
Control	0.05	0.005	0
Treatment 1	0.05	0.0025	0.00475
Treatment 2	0.05	0	0.0095

Determination of pH

pH value of model systems was measured by pH meter (Schott Gerate Model CG841, Mainz, Germany).

Determination of browning pigment formation (A₄₂₀)

The brown color was determined according to the method of Noiram (2011) by measuring the absorbance of the sucrose/sucralose/ L-lysine model system at 420 nm (A_{420}) using a spectrophotometer (UV-2101, Shimadzu, Kyoto, Japan). Melanoidins concentration was calculated by using Lambert–Beer equation (ϵ =1 L mmol⁻¹ cm⁻¹).

Determination of L*, a*and b* values

The visual color change of sample was measured by using a spectrophotometer (Hunterlab Model Color Quest® XE, USA). The measurement was set up under D65 (day-light) light source, large viewing area (1 inch. diameter) and the observer at 10°, (CIE, 1978). The CIE Lab parameters, namely "L*" (lightness; white, 100: black, 0), "a*" (redness; red, +: green, -) and "b*" (yellowness; yellow, +: blue, -) were determined by means of the Universal software. The colorimeter was standardized against a standard white tile on RSIN mode.

Determination of sugar contents

Sucrose, glucose and fructose contents were measured by the method of AOAC 982.14. Sugar contents were analyzed by using HPLC (Waters, Milford, MA, USA) with Sugar-Pak column (size 6.5x300mm,, USA). The mobile phase was HPLC grade water. Flow rate was 0.5 ml/min and the sample injection volume was 10μ l. The temperature was controlled at 90° C and the detector was Reflective Index (RI) detector.

Kinetic modeling

The rate of reactant degradation and browning pigment formation during heating was modeled using equation 1.

$$dC/dt = -kC^n$$
 (eq. 1)

where C is concentration of reactant (mmol/l), t is time (min), k is reaction rate constant and n is kinetic order of the reaction. The model was determined by using the differential method. The best fitted of the model was determined by the correlation coefficient (R²). Temperature dependence of reaction rate constant was determined using linear and exponential correlations.

RESULTS AND DISCUSSION

Changes of sugar contents

Sucrose, glucose and fructose concentration of the model system are

shown in Figure 1. Noted that the sugar content of sample with ratio of sucrose (M): sucralose (mM) of 0:0.0095 is not shown in this Figure 1 because there is no sucrose in the system and sucralose is not analyzed. From Figure 1a and d, sucrose loss increased as heating time and heating temperature increased. Moreover, the increasing of sucrose content resulted in higher sucrose loss and accumulation of glucose and fructose contents. Loss of sucrose was due to the degradation of sucrose to glucose and fructose. Panpae *et al.* (2008) studied the effects of temperature (30, 70 and 80°C) and pH (3, 5, 7 and 11) on sucrose loss in sucrose solution. The results showed that loss of sucrose content increased when time, temperature and acidity increased.

Figure 1b, 1c, 1e and 1f show that, glucose and fructose were accumulated in the system when heating time increased except at 70°C. Similar results were reported by Bands *et al.* (2003) in which galactose and glucose increased when heating time increased in lactose-casein system. At higher temperature, glucose and fructose



Figure 1 Sucrose, glucose and fructose content of the sucrose-sucralose-lysine model system prepared with various ratio of sucrose (M): sucralose (mM) of 0.005: 0 (**a**,**b**,**c**) and 0.0025: 0.00475 (**d**,**e**,**f**) during heating at $70(\triangle)$, $80(\triangledown)$, $90(\bigcirc)$ and $100(\bigcirc)^{\circ}$ C for 48 hours.

accumulation were higher. The result also showed that, the accumulation of glucose was higher than fructose. This could be because fructose has higher rate of Maillard reaction than glucose (Rattanapanone 2008). At 70°C, glucose and fructose were not detected in the system. This might be because glucose and fructose were immediately converted to other chemicals in Maillard reaction. It might be stated that the browning reaction at low temperature was controlled by the rate of sucrose degradation.

Changes of browning pigment and color

At Figure 2a, 2b, 2c and 2d, A_{420} of all samples increased when sucrose content, heating temperature and heating time increased. The increase of ratio of sucrose to sucralose resulted in the increase of A_{420} . Similar results were reported by Martins *et al.* (2005b) in which A_{420} increased with increasing temperature in glucose-glycine model system with pH value of 6.8 and heating temperature of 80-120°C. Matmaroh *et al.* (2006) reported that A_{420} the fructose-glycine model system increased with increasing reactant concentration. The increase of A_{420} represented the increase of brown pigment formation that affected color of the model system. The result showed that the increase of A_{420} led to the decrease of L^{*}, a^{*} and increase of b^{*}.

Noted that, in the system which had only sucralose (Figure $2(\mathbf{v})$), browning pigment was formed. Sucralose could be a cause of browning reaction because at low temperature of 25°C and pH of 3.0, sucralose could break down to 4-chloro-4-deoxy-galactose (4CG) and 1,6-dichloro-1,6dideoxyfructose (1,6DCF) (Binns 2003; Rahn 2010). 4CG and 1,6DCF also have a reducing point as glucose and fructose when they are broken down from sucrose. The results also showed that browning pigment formation from sucralose were lower than those of sucrose at the same sweetness value (0.005: 0 and 0: 0.0095) as shown in Figure 2(a-d).

Changes of pH

The initial pH of model system was at 6.0.The results showed that the pH of all model systems were constant throughout the study. Similar results were reported by Matmaroh *et al.* (2006) who studied the effect of reactant concentration on Maillard reaction in fructose-glycine model system. It was reported that the rate of decrease of pH was higher at higher fructose concentration. The decrease of pH was found at the concentration of fructose above 4.5 mM.

Kinetic modeling of sugar reduction and browning pigment formation

To understand the browning reaction in the model system, kinetic model was used to predict the phenomena of reactants and product changes during heating. In this research, L-lysine was presented in excess and sucrose was a limiting substrate for Maillard reaction. In this work sucralose was used in a very low amount (mM) when comparing to sucrose (M). The model mechanism of browning reaction in sucrose-sucralose-lysine model system was shown in the schematic diagram 1.



Schematic diagram 1 Irreversible reactions in series for the browning pigment formation in sucrose/sucralose/L-lysine model system.



Figure 2 Browning pigment formation of sucrose-sucralose-lysine model system prepared with various ratio of sucrose (M): sucralose (mM) of 0.005: 0 (\bullet), 0.0025: 0.00475 (\circ), 0: 0.0095 (\mathbf{V}) during heating at 70 (**a**), 80 (**b**), 90 (**c**) and 100°C(**d**) for 48 hours.

To fit the kinetic model to the experimental data, the reaction in schematic diagram 1 was converted to the differential equation. In the proposed reaction, the rate of change of sucrose, glucose, fructose and melanoidins are written below:

d[sucrose]/dt	$= -k_1 [sucrose]^n$	(eq. 2)		
d[glucose]/dt	$= k_1 [sucrose]^n - k_2 [glucose]^n$	(eq. 3)		
d[fructose]/dt	$= k_1 [sucrose]^n - k_3 [fructose]^n$	(eq. 4)		
d[intermediate]/dt = k_2 [glucose] ⁿ + k_3 [fructose] ⁿ - k_4 [intermediate] ⁿ				
		(eq. 5)		
$d[Melanoidins]/dt = k_4 [intermediate]^n$		(eq. 6)		
Where k_1, k_2, k_3, k_4 are rate cor	nstant and n is a reaction order	r.		

Sucrose degradation, glucose & fructose formation and browning pigment formation could be described by zero-order reaction in series kinetic with the high R² as shown in Figure 3. From the result, it was indicated that the increase of temperature led to a higher loss of sucrose, higher glucose & fructose accumulation and browning pigment formation. The rate constant of sucrose loss and browning pigment formation were increased when the temperature and

sucrose content increased. The rate constant of glucose (k_2) and fructose (k_3) loss were decreased when the temperature increased. This might be due to the rate of browning pigment formation was lower than the rate of glucose and fructose formation leading to glucose and fructose accumulation in the system. The maximum rate constant of browning pigment formation of model system was found at higher sucrose content and higher temperature.

Temperature dependence of the rate constant of sucrose & fructose loss and browning pigment formation could be described by the exponential equation as shown in Figure 4a, 4c, 4d. Linear equation was used to describe the temperature dependence of the rate constant of glucose loss as shown in Figure 4b. The results of prediction are shown in Figure 5. The results indicated that percentage deviation (P (%)) between the experimental and predicted values of sucrose, glucose, fructose and browning pigment were range 4.60-12.95, 1.06-9.95, 0.26-5.21 and 0.29-1.69, respectively. Although, the deviation values of sucrose loss at highest sucrose content were slightly higher than 10%, this kinetic model was accepted considering the complexity of the browning reaction.



Figure 3 Curve fitting of zero-order kinetic model to experimental data for sucrose degradation, glucose & fructose formation and browning pigment formation of treatment prepared with ratio of sucrose(M): sucralose(mM) of 0.005: 0 (a) and 0.0025: 0.00475(b) during heating at $100^{\circ}C(^{\circ})$, $90^{\circ}C(^{\circ})$, $80^{\circ}C(^{\circ})$, and $70^{\circ}C(^{\circ})$ for 48 h.



Figure 4 Temperature dependence of the rate constant of sucrose (**a**), glucose (**b**), fructose (**c**) loss and browning pigment formation(**d**) in model system prepared with various ratio of sucrose: sucralose of 0.005: 0 (•) and 0.0025: 0.00475(O).

CONCLUSION

Kinetic of browning pigment formation and reactants consumption of Maillard reaction in sucrose-sucralose-lysine model system at various ratios of sucrose to sucralose were studied. For the model system, sucrose was replaced by sucralose in order to decrease the changes of browning pigment formation and L^{*}, a^{*}, b^{*} values. The pH values of all treatment were constant throughout the studies. Zeroorder reaction in series kinetic could describe sucrose, glucose, fructose consumption and browning pigment formation in model system. Temperature dependence of the rate constants of sucrose and fructose reduction and brown color formation could be described by exponential equations. Linear equation was used to describe the temperature dependence of the rate constant of the loss of glucose.

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Figure 5 Kinetic model validations for sucrose, glucose, fructose loss and browning pigment formation as shown in schematic diagram 1 of model system prepared with various ratio of sucrose: sucralose of 0.005: 0 (**a**) and 0.0025: 0.00475 (**b**). Simulation and experimental data are represented by dash line and symbol, respectively at 100°C (^O), 90°C ([△]), 80°C ([□]), and 70°C ([◇]) for 48 h.